PROCEEDINGS

OF THE

AMERICAN ACADEMY

OF

ARTS AND SCIENCES.

VOL. XXX.

PAPERS READ BEFORE THE ACADEMY.

AID IN THE WORK DESCRIBED IN THIS PAPER WAS GIVEN BY THE ACADEMY FROM THE C. M. WARREN FUND FOR CHEMICAL RESEARCH.

I.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE CASE SCHOOL OF APPLIED SCIENCE.

XIX. — ON THE DETERMINATION OF SULPHUR IN VOLATILE ORGANIC COMPOUNDS.*

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Presented April 11, 1894.

THE great quantity of products introduced into the petroleum industry from the fields in Ohio and Canada yielding the sulphur oils has involved many sulphur determinations, and the necessity of a rapid method capable of affording results of extreme accuracy, especially in oils containing a small fraction of one per cent of sulphur. Several of the older methods leave nothing to be desired in point of accuracy, but they are not sufficiently expeditious for service in manufacturing operations, or in investigations which depend upon immediate information concerning the percentage of sulphur.

The first attempt to determine sulphur in organic compounds by combustion in oxygen was made by C. M. Warren,† the sulphuric acid formed being absorbed within the combustion tube in plumbic peroxide.

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* This paper is one of the series on the composition of the sulphur petroleums.

† These Proceedings, VI. 472.

The oxides and acids formed by combustion were first distilled and collected in bromine water as an oxidizing agent by Sauer * and this method was still further improved by Mixter, † who avoided the use of a rubber cork in the forward end of the combustion tube, carried forward the volatilized substance by a current of carbonic dioxide, and suggested more efficient means for oxidation by bromine and absorption. All these methods depend upon the formation of sulphuric acid and precipitation as baric sulphate, which involves considerable labor when a large number of determinations are necessary in a limited time. To overcome this difficulty Burton ‡ suggested a modification of the method of Sauer, which consists in absorbing the oxidized sulphur in a standard solution of potassic hydrate and titrating the excess of alkali with standard sulphuric acid.

Besides these methods the only other suitable means for the determination of sulphur in oils with large percentages of sulphur is the well known method of Carius, in which the substance is oxidized in a closed tube by means of fuming nitric acid. In its applicability to all classes of compounds, and in the accuracy of results of which it is capable, this method leaves little to be desired except perhaps in the analysis of oils containing less than one hundredth of one per cent of sulphur. On account of the limited weight of substance that can be oxidized in a Carius tube another method must be selected for substances containing less sulphur. Our experience has shown that the Carius method may be relied upon in sulphur determinations to yield concordant results within a few hundredths of one per cent. Oxidation of the less volatile oils containing a small percentage of sulphur, without doubt, may be accurately accomplished in an open vessel, but with larger amounts of sulphur the action of nitric acid is so violent that it must entail loss by volatilization, unless indeed the sulphur oil is considerably diluted by a sulphur-free oil, in which case the solvent must be completely oxidized.

The great number of sulphur determinations in crude oils and products obtained from them, connected with the extended examinations which have occupied my attention during several years past, has demanded a careful comparison of the various methods as to their efficiency and economy of time. Particular attention has been given to details of the Carius method, with the precautions necessary in its successful application to the analysis of sulphur oils. The first requi-

* Fres. Zeit. Anal. Chem., XII. 32.

† Amer. Chem. Journ., II. 396.

‡ Ibid., XI. 72.

site is a furnace of suitable construction to maintain an equal temperature, easily controlled in all the tubes within the furnace, without a great loss of heat by radiation. For this purpose and for Carius analyses in general I have recently had a furnace constructed which differs in certain features from any other I have seen, and it shows such a high degree of efficiency that a brief description may not be entirely devoid of interest. The body is of the ordinary cylindrical form, 75 cm. long and 25 cm. in diameter, of heavy sheet iron, and it is surrounded by two outer jackets of sheet iron each enclosing a half-inch space, and extending beneath on either side to within 6 cm. of the heating tube; it is supported upon legs of strap iron three sixteenths of an inch thick and two inches wide, each entirely encircling the body at either end for rigidity. These two air spaces retain the heat so effectually that the hand may be borne on the outside of the furnace when the thermometer within indicates a temperature of 200°. The iron tubes are as usual of gas pipe, with threads at either end with caps easily movable by the fingers. With a small hole in each cap for the escape of gas, these tubes retain all glass in the most violent explosions. When several tubes are in the furnace at the same time a record of them may conveniently be kept by suspending metal tags numbered consecutively from the holes in the caps by means of bent wire.

Figure 1 shows the arrangement of the outer air spaces with the position of the heating tube. The furnace is heated by means of a gas stove heater 45 cm. in length, with thirty-two gas jets that will burn continuously with a flame 2 mm. high, giving a temperature within the furnace of less than 60°; by interposing an asbestos or an iron plate a considerably lower temperature may be maintained. The heating tube is supported on two iron straps bolted to the legs, one at either end of the furnace; by means of it the heat is very equally distributed with little waste, and the glass tubes being thus evenly heated there is less danger of loss by explosion. A temperature of 200° may be obtained within twenty-five minutes after lighting the jets, and it may be maintained with jets fifteen millimeters in height, requiring a small consumption of gas; the hand may be held without discomfort for some time directly beneath the heater. The variation in temperature at different heights within the furnace is small; with the thermometer at 275° at the level of the upper tubes, the tempera-

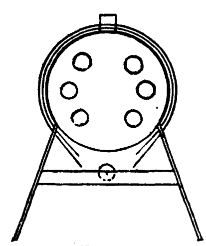

FIG. 1.

ture at the level of the lower tubes is about 9° higher. For temperatures higher than 275° a second heating tube is necessary.

It is frequently convenient to be able to regulate within close limits the flow of gas for the required temperature without further attention after lighting the jets. The device shown in Figure 2, which suggested itself for this purpose, consists in attaching to the end of the gas valve by means of a screw thread a brass cap with an index of stout copper wire moving in front of a graduated circle with a radius of about six inches.

With glass tubes of large size, — those we use are 1.5 mm. inside diameter, — well sealed and with strict adherence to certain conditions which have elsewhere been described by A. W. Smith and me,* there is little danger of an explosion. The quantity of nitric acid should not be in excess of twenty times the weight of the substance taken, and after heating to 175° for fifteen hours the tubes are opened, — best without removing from the furnace, — resealed and heated again to 250° during five to ten hours. The serious objection to the Carius method for sulphur is the slow process of oxidation, and it seems hardly possible to hasten the operation by raising the temperature, since glass tubes will not stand the great pressure.

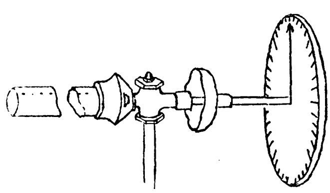

FIG. 2.

In studying various methods depending upon the oxidation of sulphur by combustion I have found that nothing less than complete oxidation gives reliable results. Many experiments on fractional combustion have shown clearly that compounds with high percentages of sulphur do not yield concordant results, even when the sulphur compound is diluted with a sulphur-free oil. I have found Burton's adaptation of the Sauer method reliable and expeditious, and with certain modifications presently to be described it is perfectly satisfactory for the analysis of oils of high as well as low percentages of sulphur. In Figure 3 the inlet tube for oxygen or air is shown as entering through the rear stopper, as proposed by Mixter, and extending just to the centre of the constriction. In the combustion of some of the oils which we have under examination, the temperature must be maintained as high as the most infusible Bohemian glass will stand, and at such temperatures the smaller tube within is distorted if it is

* Amer. Chem. Journ., XVI. 83

placed in the forward portion of the combustion tube in the zone of greatest heat; if it terminates at the narrowest point of the constriction, continuous combustion is insured by thorough admixture of the volatilized substance with oxygen. Complete oxidation is still more certain in rapid combustion if that portion of the tube in front of the narrower part is left somewhat longer than is preferred by Sauer, Mixter, or Burton. The tubing we have in use is somewhat thicker in the wall than that in ordinary use, and larger, with an inside diameter of 18 mm. It is important that the oxidation proceed as rapidly as is consistent with complete absorption, and we find that this is best accomplished in a large U tube partly filled with broken glass. Our U tube is 34 cm. in height, 25 mm. inside diameter, and with 50 c. c. of the absorbent solution a rapid gaseous stream may be passed through without danger of loss. For low sulphur oils we use a solution of sodic hydrate of such a strength that 1 c. c. equals 0.0010 gram of

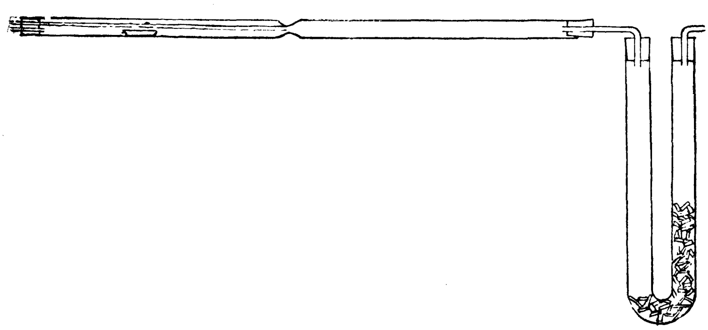

FIG. 3.

sulphur, and for higher percentages a solution in which 1 c. c. equals 0.0050 gram. Methyl orange has been used as an indicator in all our determinations; the change in color in titrating an alkaline solution with this indicator is well defined and exceedingly delicate. The titrations may be made in the U tube without transferring the solution after washing in the acid from the combustion tube. To carry forward the volatilized substance it is advantageous to introduce a slow current of carbonic dioxide, as proposed by Mixter, and we have sometimes used a combustion tube closed with a rubber cork in front and sometimes a bent tube. With substances containing a high percentage of sulphur it is doubtless safer, as Mixter suggests, to avoid the use of a cork in front.

On account of the large consumption of oxygen in burning rapidly a considerable weight of oil, — at least three times the quantity theoretically required for oxidation, — and finding that the combustion proceeds with equal facility in air, nearly all our determinations have been made in a current of air supplied under pressure, with the same means for exhaustion that Burton found advantageous. The operation requires close attention and 0.5 to 1 gram of oil may easily be burned in forty-five minutes to one hour, depending upon the nature of the substance, the heavier oils especially if containing much sulphur being the most difficult to burn. The higher sulphides will not support a continuous flame, and dependence must be placed upon a very hot tube; with the more volatile oils it is sometimes difficult to maintain a continuous flame even in oxygen, the combustion proceeding in long intermittent non-luminous flashes. If the flame becomes luminous the rapidity of volatilization must be instantly checked, and the flow of air increased. The appearance of white fumes in the forward part of the combustion tube or the absorption tube, indicating improper adjustment as to the temperature, flow of gas, or rate of volatilization, is invariably attended with low results. The completeness of the absorption in the U tube was tested by placing a second tube beyond it containing a similar solution, but no trace of acid was found in the second tube when the excess of alkaline hydrate in the first at the end of the analysis was not less than 15–20 c. c. With a smaller excess in rapid combustions there is danger of loss. The oil for analysis is weighed in a bulb or tube of hard glass, and it is sometimes convenient to transfer most of it to a platinum or a porcelain boat, which may easily be accomplished without loss within the combustion tube provided there is a gentle current of air inward and the combustion tube in front has previously been heated to the required temperature.

In the examination of Ohio and Canadian sulphur petroleums for identification of the paraffine, aromatic, and unsaturated hydrocarbons, sulphur compounds, and other constituents, with which I am at present engaged, numerous determinations of sulphur have been necessary, and the extreme convenience of combustion in air has greatly facilitated the separation of the various products. As an evidence of the reliability of this method, the following results are selected with parallel determinations by the Carius method: —

	Percentage of Sulphur. Combustion in Air.	Percentage of Sulphur. Carius.
Distillate from crude Canada oil collected at 89°–91° after one distillation under 50 mm. and seven under atmospheric pressure	0.044	0.043
Distillate from crude Ohio oil collected at 127°–129° after one distillation under 50 mm. and seven under atmospheric pressure	0.0343	0.036
Distillate from crude Canada oil collected at 115°–117° after one distillation under 50 mm. and seven under atmospheric pressure	0.173	0.0108
Distillate from crude Canada oil collected at 120°–130° after one distillation under 50 mm. and five under atmospheric pressure	0.505	
The same after shaking five times with alcoholic mercuric chloride	0.07	
The same after shaking once with alcoholic mercuric chloride with the addition of solid mercuric chloride	0.086	
Sulphur oil from Canada sludge acid . . .	I. 6.3 II. 6.3	6.47
Sulphur oil from Canada sludge acid . . .	17.36	17.31
Sulphur oil from Canada sludge acid . . .	I. 16.67 II. 16.76	
Canada sulphur oil	6.15	6.01
Canada sulphur oil	13.67	13.70
Crude sulphide separated by mercuric chloride from fraction 110°–115° of sulphur oil after the fifth distillation under 50 mm.	18.85	
A fraction of the same corresponding to pentyl sulphide, percentage of sulphur, 18.39		I. 18.53 II. 18.55 III. 18.67

These results were obtained by six persons working independently of one another.

The oxidation of nitrogen to any considerable extent by the use of air in the combustion of sulphur compounds is evidently excluded by the close agreement of the results it yields with corresponding determinations by the Carius method. In accordance with the suggestion of a friend, from the fact that nitrous and nitric acids are formed to a greater or less extent depending upon conditions in the ordinary forms of combustion, it seemed of interest to ascertain whether these acids were present at all in the alkaline absorbent. In testing for the formation of nitrous acid, the exceedingly delicate color reaction was applied which is produced in an acid solution of a nitrite by the addition of sulphanilic acid and naphthylamine chloride. An

examination of our reagents showed that the purest commercial sodic or potassic hydrate gives an intense color, and even hydrates prepared from the metals are not free from color. Pure sulphuric acid gave no reaction, and pure sodic carbonate only a faint color. We finally obtained a solution that gave not a trace of color by dissolving metallic sodium and boiling the solution for some time with metallic aluminum. With this solution as the absorbent in a combustion of a sulphur oil, after the analysis the solution was as free from color as before when it had stood half an hour after the addition of the reagents. Since a pink color is distinctly visible in this reaction with one part of nitrogen in the form of nitrous acid in one thousand million parts of solution, it is safe to conclude that nitrous acid is not one of the products in this form of combustion.

To determine whether nitric acid is formed, after the combustion a portion of the sodic hydrate solution was neutralized, mixed with ferrous sulphate, and concentrated sulphuric acid poured beneath the solution. No color was visible at the junction of the two liquids. In a second test another portion of the alkaline solution was nearly neutralized with sulphuric acid, evaporated to dryness, and a few drops of phenolsulphuric acid added. Upon diluting to a definite volume, no difference could be perceived between the color of this solution and that given by phenolsulphuric acid alone in a blank experiment. In the combustion of sulphur oils in air, therefore, the atmospheric nitrogen is not affected.

For efficient aid in studying the details of these methods of analysis, I should acknowledge my obligations to Mr. W. O. Quayle, and to my assistants, Messrs D. B. Cleveland and G. M. Little.